

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

July 25, 1995

3. REPORT TYPE AND DATES COVERED

Technical Report 06/01/94 - 05/31/95

4. TITLE AND SUBTITLE

Anodization of Copper Microelectrodes in a Complexing Medium: Determination of Stability Constants of Products.

5. FUNDING NUMBERS

Grant: N00014-93-1-0375-1

R&T Code: 3133043

Dr. Robert J. Nowak

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report No. 1

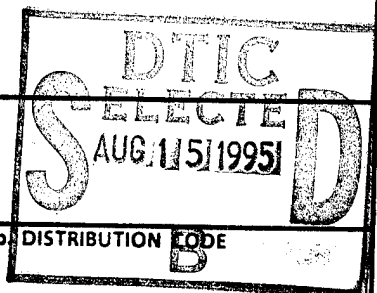
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
Chemistry Division
800 North Quincy Street
Arlington, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

To be published in Analytical Chemistry



12a. DISTRIBUTION/AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

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13. ABSTRACT (Maximum 200 words)

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19950814 005

14. SUBJECT TERMS

Copper, chloride, formation constant, microelectrode, pulse voltammetry

15. NUMBER OF PAGES

40

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

OFFICE OF NAVAL RESEARCH

GRANT: N00014-93-1-0375-1

R&T Code 3133043

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Anodization of Copper Microelectrodes in a Complexing Medium:
Determination of Stability Constants of Products

by

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Prepared for Publication

in

Analytical Chemistry

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July 25, 1995

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ANODIZATION OF COPPER MICROELECTRODES
IN A COMPLEXING MEDIUM:
DETERMINATION OF STABILITY CONSTANTS OF PRODUCTS.

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Abstract- A model is presented for the anodization of a metal electrode by normal pulse voltammetry in complexing medium. The analysis is based on analytical expressions for current during normal pulse voltammetry at a microelectrode. It is applied to the anodization of a copper microdisk electrode in aqueous chloride solutions. Optimization of the fit of the model to the data yields the overall formation constants of CuCl (K_1) and CuCl_2^- (β_2) as $\log K_1 = 2.93 (+ 0.02, - 0.05)$, and $\log \beta_2 = 5.54 (+ 0.12, - 0.17)$. These values agree with those found in the literature. The advantages of this analysis over traditional approaches which employ an approximation of small current are described.

Key words: Copper, chloride, formation constant, microelectrode, pulse voltammetry

INTRODUCTION

Previous reports have demonstrated the advantages afforded by electrodes of very small dimension for studies of processes associated with corrosion. The steady-state is achieved at short times, and high current densities are attainable with minimal ohmic polarization.¹⁻⁴ At sufficiently short time, the amount of metal anodized is small in comparison with the electrode dimension, and thus measurements can be made with little damage to the electrode.

When a metal electrode is anodized in a ligand-containing solution, the general reaction can be written as



where the number of ligands per metal ion is given by p . The product, $MX_p^{(mp-n)-}$, is referred to as the pth complex. The overall formation constant of the pth complex, β_p , is given by

$$\beta_p = (MX_p^{(mp-n)-}) / (M^{n+})(X^{m-})^p \quad (2)$$

Fick's law is used to write steady-state current as a function of the concentration of the reacting species as

$$\begin{aligned} i_{ss} &= (n/p)FAD_X(\partial C/\partial x)_s \\ &= (n/p)FAD_X([X]_s - [X]_o)/\delta \end{aligned} \quad (3)$$

This current is negative for an oxidation, according to convention. The subscript s is used to indicate that the quantity is evaluated at the electrode surface. Bulk values will be denoted with the subscript o . At a microdisk electrode, the diffusion layer thickness, δ , is given by $\pi r/4$, where r is the radius of the electrode. When more than one reaction occurs at the electrode surface, this expression for steady-state current is complicated if written in terms of the flux of the complexing ligand. By definition, at the electrode the flux of products is equal and opposite to the flux of reactants under steady-state conditions. Thus we may rewrite eq 3 as

$$i_{ss} = -[4(n/p)FD_r] \sum_p p ([MX_p^{(mp-n)-}]_s - [MX_p^{(mp-n)-}]_o) \quad (4)$$

where we have assumed that all diffusion coefficients are equal in value. In the present case the initial bulk concentration of each product, $[MX_p^{(mp-n)-}]_o$, is zero. Eliminating that term and making use of the overall formation constants from eq 2,

$$i_{ss} = -[4(n/p)FD\gamma] \sum_p \beta_p \theta(\gamma_X^p / \gamma_{MXp}) p [X^{m-}]_s^p \quad (5)$$

where $\theta = \exp [nf(E - E^0)]$, and $f = F/RT$. The activity coefficients of the various species are denoted by γ . The assumption inherent in this equation is that the chemical processes described by the constants β_p are in equilibrium.

Aoki and Osteryoung⁵ have provided an equation which relates current at near-steady-state conditions to steady-state current through a dimensionless parameter $P = 4Dt_p/r^2$, where t_p is the pulse time. The current, i_{NP} , after a potential pulse is

$$i_{NP} = i_{ss} f(P) \quad (6)$$

where $f(P)$ is given by

$$f(P) = 1 + 0.71835P^{-1/2} + 0.05626P^{-3/2} - 0.00646P^{-5/2} \quad (7)$$

for $P > 0.88$. This equation works best when the value of $f(P)$ is close to 1, which is when P is large, that is, the diffusion layer thickness is large in comparison with the size of the electrode.

In previous work, we have employed steady-state polarization as a technique for studying the anodization of metal electrodes.¹ Experiments were carried out by means of a staircase waveform with a period of 2 s. For typical values of r , say 12.5 μm , the value of $f(P)$ is 1.07, and the steady-state is nearly achieved. However, by employing a normal pulse waveform of approximately the same period, equivalent data can be obtained somewhat more rapidly, more reproducibly, and with somewhat less damage to the electrode. For the data considered here, the normal pulse waveform was used with pulse width of 50 ms and time between the pulses of 1 s. Under these conditions, $f(P) = 1.46$,

that is, the experiment approaches the steady-state on each pulse. Between pulses the potential of the electrode is held at a negative value where the surface is conditioned and the initial conditions in solution are restored.

The value of $f(P)$ is independent of the potential and therefore constant for the entire voltammetric wave. In other words, the shape of the voltammetric wave is not affected by deviation from the steady-state.

The system we have chosen to investigate is anodization of copper in aqueous chloride solution. Our interest is spurred by the importance of corrosion of copper in various media, including seawater.⁶ We wish to understand and characterize the chemical processes involved in the anodic dissolution of copper and the factors which accelerate or impede corrosion. The first step to this end is to develop a rigorous and reliable method for analyzing data obtained in these systems.

When copper metal is anodized in aqueous chloride solution, the reactions can be expressed as



Many Cu(I)-chloride complexes are known. In the range of chloride concentrations from 0.05 to 1.0 M, the predominant species is the second complex, CuCl_2^- . The first complex, CuCl , becomes more favored as the chloride concentration is decreased, and the third complex, CuCl_3^{2-} , becomes more favored as the concentration of chloride is increased.⁷ In this analysis, only the first two complexes are taken into account, that is, $p = 1$ and $p = 2$.

The anodization experiments described here were done with no anion present except chloride. Thus these experiments were performed without supporting electrolyte. In general, there are two purposes for addition of supporting electrolyte in electrochemical experiments: to ensure sufficient conductivity of the solution, and to suppress migration. In these experiments, the bulk concentration of chloride is high enough that resistivity of

the solution is not a problem. Migration, however, influences transport of reactants. In the following treatment, migration is assumed to be negligible. The effect of migration is considered in the discussion of experimental results.

Following the development of eqns. 5 - 8, we can express the total current as a sum of two individual currents, i_1 and i_2 , as

$$i_1 = i_{NP,1} = -(4nFDr)f(P)K_1\theta(\gamma_{Cl}/\gamma_{CuCl})[Cl^-]_s \quad (9)$$

$$i_2 = i_{NP,2} = -(4nFDr)f(P)\beta_2\theta(\gamma_{Cl}^2/\gamma_{CuCl_2})[Cl^-]_s^2 \quad (10)$$

for $p = 1$ and $p = 2$, respectively. These currents are made dimensionless by division by the limiting current, $-(4nFDrC)f(P)$, where C is equal to $[Cl^-]_0$. The resulting dimensionless current functions are

$$\psi_1 = K_1\theta(\gamma_{Cl}/\gamma_{CuCl})([Cl^-]_s/C) \quad (11)$$

$$\psi_2 = \beta_2\theta(\gamma_{Cl}^2/\gamma_{CuCl_2})([Cl^-]_s^2/C) \quad (12)$$

The total dimensionless current function, ψ , is the sum of the two individual dimensionless current functions,

$$\begin{aligned} \psi &= \psi_1 + \psi_2 \\ &= (\theta/C)[(K_1x/\gamma_{CuCl}) + (\beta_2x^2/\gamma_{CuCl_2})] \end{aligned} \quad (13)$$

where $x = \gamma_{Cl}[Cl^-]_s$, which is the activity of chloride ion at the electrode surface. If we assume that the two singly-charged species Cl^- and $CuCl_2^-$ have the same activity

coefficient (γ), and that the neutral species CuCl has an activity coefficient of unity, eq 13 can be simplified to

$$\psi = (\theta/\gamma C)[K_1\gamma x + \beta_2 x^2] \quad (14)$$

It remains only to calculate the activity of chloride ion at the electrode surface. This can be done through the mass balance equation for chloride. It is at this point that it becomes necessary to assume equality of diffusion coefficients, as done in eq 4. Without this assumption one must resort to numerical methods to solve the diffusion problem.⁸

The equation for the mass balance of chloride is

$$[\text{Cl}^-]_o = [\text{Cl}^-]_s + [\text{CuCl}]_s + 2[\text{CuCl}_2^-]_s \quad (15)$$

Multiplying by γ and using the definitions of the formation constants, we obtain

$$\gamma C = x + K_1\theta\gamma x + 2\beta_2\theta x^2 \quad (16)$$

Thus,

$$x = (4\beta_2\theta)^{-1} \{[(1 + K_1\theta\gamma)^2 + 8\beta_2\theta\gamma C]^{1/2} - (1 + K_1\theta\gamma)\} \quad (17)$$

It can be shown using L'Hôpital's rule that x goes from γC to 0 as θ increases from 0 to infinity, as expected. Similarly, ψ_1 goes from 0 to 1 and ψ_2 goes from 0 to 1/2 as θ increases without bound. This is due to the fact that the limiting current expected for $p = 2$ is one-half as large as that expected for $p = 1$, since two ligands are required per electron in the former case. Equations 14 and 17 are the basis for the data analysis.

For conventional measurements at large electrodes, the current is usually limited by ohmic polarization to values much less than the diffusion-limited plateau current. Thus the approximation is usually made that $i \ll i_{\text{lim}}$. This assumption results in the familiar equation for steady-state current as a function of potential for the anodization of a metal in the presence of ligand.¹ Of course, this approximation restricts the data analysis to the region of low current, thus eliminating most of the voltammetric wave from accurate analysis. In this work, we make no such approximation.

A data analysis routine based on the above equations was composed and incorporated into the COOL algorithm,⁹ which finds optimal values of parameters by minimizing the deviation of the theoretical data points from the experimental ones. The program operates on a set of dimensionless parameters on which the value of the current function (ψ) depends. In this case, the parameters are $K_1\theta\gamma$ and $\beta_2\theta\gamma C$. Determination of these parameters yields the values of K_1 and $K_2 = \beta_2/K_1$ only if E^0 is known independently. Thus from the computational point of view it is convenient to treat $K_1\gamma$ and $\beta_2\gamma C$ as the dimensionless parameters and to require that the value of E^0 be provided prior to the analysis of data.

Using the current function, or shape function, the calculated current is fit to the experimental current, which is given by

$$i = a\psi(K_1\gamma, \beta_2\gamma C) + b + \varepsilon(0;\sigma) \quad (18)$$

A linear regression gives values of a (the slope, in amperes) and b (the current offset, in amperes). The residual, ε , is small for a good fit. According to the definition of ψ (eqs 9 - 13), the slope should equal $-(4nFDrC)f(P)$. An opportunistic search routine employing the COOL algorithm is used to find the values of the parameters which minimize the complement of the correlation coefficient of this linear relation, $(1 - R)$. These are the optimal values which maximize the correlation of theory with experiment.

We have applied this analysis to the results of Wikiel, dos Santos and Osteryoung,³ which were obtained in aqueous chloride solution by employing copper microdisk electrodes. In addition, we have measured independently under well-controlled conditions the value of E^0 in this system. In treating the experimental results we have taken proper account of the effects of activity. The results yield values of K_1 and β_2 , which can be compared with existing values in the literature. It should be clear, however, that this approach is applicable to the anodization of any metal in any complexing medium. Thus our main purpose is to present a comprehensive approach to the analysis of voltammograms obtained to characterize the primary processes in anodization of metals.

EXPERIMENTAL SECTION

Normal Pulse Voltammetry. The normal pulse voltammetric data were taken from the earlier work of Wikiel et al.³ Briefly, the copper microdisk electrodes were prepared from 25 μm -diameter copper wire (Cu: 99.99%, from Goodfellow Metals Ltd.). The copper wire was cleaned and sealed in glass as described previously.³ The electrode was polished with Texmet polishing cloth with alumina suspensions (Beuhler Ltd.) of 1.0, 0.3 and 0.05 μm grit sizes, in that order. The electrode was repolished to a mirror-like surface before each experiment.

Electrodes. A copper wire electrode was used in the potentiometry experiments. The copper wire was rinsed with water (see next section) and placed in the plating solution (0.37 M CuSO_4 + 1.4 M H_2SO_4). Immediately prior to use, the copper wire was rinsed with copious amounts of water. Its appearance was bright and uniform, with no visible discoloration due to surface oxides.

A glassy carbon-glassy carbon rotating ring-disk electrode (EG&G PARC Model RDE0032) was used to study the copper reproportionation reaction. The disk radius was 2.81 mm. The inner radius of the ring was 3.12 mm, and the outer radius was 4.20 mm.

This corresponds to a geometric factor (N) of 0.422. The glassy carbon surfaces were polished with alumina suspensions on a polishing cloth as was the copper microelectrode described above. After polishing, the electrode was rinsed thoroughly with water. The rotation rate was controlled with a Ring-Disk Electrode System (EG&G PARC Model 636).

In all experiments, a saturated calomel reference electrode (SCE, EG&G PAR K0077) and a platinum flag auxiliary electrode were employed. Both the reference and auxiliary electrodes were isolated from bulk solution by placing them in separate fritted compartments. When not in use, the SCE was stored in a vial containing saturated sodium chloride solution.

Instrumentation and Chemicals. An EG&G PARC Model 273 potentiostat was used in all electrochemical experiments. All reagents were used as received (reagent grade) without further purification. All solutions were made with distilled water which was passed through a Millipore Milli-Q purification system. This water was also used in cleaning electrodes and electrochemical cells before experiments were performed. All solutions were purged thoroughly with argon gas for at least 20 minutes before use in experiments, and during experiments argon was passed over the solution.

The programs were written in FORTRAN (Lahey FORTRAN 77) on a Gateway 2000 PC computer.

Procedures. There are three separate types of experiments included in this report: rotating ring-disk experiments, potentiometry and normal pulse voltammetry at a microelectrode. The third was described in a previous report.³

In the rotating ring-disk experiments, copper was first plated onto the disk electrode from the deaerated plating solution ($0.37 \text{ M CuSO}_4 + 1.4 \text{ M H}_2\text{SO}_4$). This was done by holding the disk potential at -0.1 V vs. SCE for three minutes, as the electrode

was rotated at 100 rpm. The ring electrode was not connected. Under these conditions, copper was plated on the disk at a slow rate to form a bright deposit, which to the eye appeared to be uniform. When deposition was performed at more negative potentials, copper was plated more quickly, but frequently the color of the deposit was not uniform over the area of the disk electrode. After the plating was completed, the disk electrode was disconnected and the ring electrode was connected. The rotation rate was adjusted to the desired initial rate, and the potential was held at +0.55 V vs. SCE. This potential is positive enough to effect the conversion of Cu^+ , which is produced at the disk by the copper reproporationation reaction, to Cu^{2+} at the ring electrode. At intervals of 20 s, the rotation rate was changed by increments of 100 rpm, e.g., from 100 to 200 rpm.

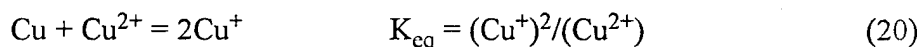
Open circuit potentials were measured between a copper wire electrode and the SCE reference electrode. The solutions tested were of dilute (1 to 5 mM) CuSO_4 , held to approximately constant ionic strength by addition of H_2SO_4 . These solutions were carefully deaerated before use. Typically the open circuit potentials were measured until they were constant for 20 minutes. The temperature of solution was $23 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

Determination of $E^\circ(\text{Cu}^{2+}/\text{Cu})$. It was necessary to obtain a value of the standard potential of the Cu^+/Cu couple, hereafter referred to as E°_1 , in the absence of complexing ligand. This is not straightforward, since equilibrium concentrations of cuprous species are very low in the absence of strongly complexing ligands such as halides and cyanide. It was determined that the best way to evaluate E°_1 was to determine by potentiometry the standard potential of the Cu^{2+}/Cu couple, E°_2 , and then relate it to E°_1 by the relationship:

$$E^\circ_1 = E^\circ_2 - (1/2f) \ln K_{\text{eq}} \quad (19)$$

where K_{eq} is the equilibrium constant of the reproporationation reaction,



Thus, E°_2 and K_{eq} must be determined in order to find E°_1 . Values of E°_1 and E°_2 are available in the literature. However the reported values cover a broad range of potentials, and therefore an accurate value cannot be picked confidently.¹⁰ We also wished to develop a general procedure that would make it possible to determine E°_1 in various solvents. Finally, we considered it prudent to make an independent measurement.

Activity coefficients were calculated for the solutions used in the potentiometry experiments by means of Bromley's method.^{11,12} Bromley's equation for the logarithm of the activity coefficient of an ion is

$$\log \gamma_i = -Az_i^2 I^{1/2} / (\rho^{1/2} + I^{1/2}) + \\ (0.06 + 0.6B)z_i^2 I / [\rho + (1.5I/z_i^2)]^2 + BI/\rho \quad (21).$$

where A is the Debye-Hückel constant (typically equal to 0.512 in aqueous solution), z_i is the charge on the ion, ρ is the solution density, B is the Bromley coefficient for the ion and I is the ionic strength in molar units. This equation is estimated to be accurate up to ionic strengths of 6.0 M. Calculated activity coefficients for Cu^+ and Cu^{2+} appear in Table I. Three sets of solutions were made with various concentrations of CuSO_4 , with ionic strengths of 60 mM, 30 mM and 20 mM, with H_2SO_4 . There was no systematic error introduced by using the three different ionic strengths, indicating that the calculated activity coefficients account adequately for ionic strength.

Figure 1 shows the results of the potentiometry experiments. The open circuit potential of the clean Cu wire electrode is plotted against the logarithm of the activity of Cu^{2+} . The data show good linearity ($R^2 = 0.97$), with a slope of 33.4 mV per decade.

Extrapolation of the line to unit activity yields a value of E°_2 of 0.099 (± 0.0050) V vs. SCE. This lies in the range of values in the literature, which is 0.095 to 0.101 V vs. SCE.¹⁰ (The standard deviation comes from the statistics of the regression analysis.)

Determination of K_{eq} . The equilibrium constant of the reproporation reaction (K_{eq}) was calculated using the rotating ring-disk method of Tindell and Bruckenstein.¹³ Copper(II) ions in bulk solution undergo reproporation with copper(0) atoms on a copper-plated glassy carbon disk. This was done in the plating solution, which was 0.37 M CuSO_4 + 1.4 M H_2SO_4 . The copper(I) ions that are produced by the reproporation were detected at the ring by oxidation to copper(II). The ring electrode was held at +0.55 V and the current was measured as the rotation rate was stepped from 100 to 900 rpm or 1100 to 1900 rpm, in increments of 100 rpm. Figure 2 shows a typical result of this experiment. The results of several experiments were averaged, and the current change was plotted versus the change in the square root of rotation rate, as shown in Figure 3. The results give a value of K_{eq} , according to eq 22, which is from ref 13:

$$K_{eq} = 2i^2k^2/(2C-ikd) \quad (22)$$

where i is the current measured at the ring electrode, C is the bulk concentration of Cu^{2+} , d is given by

$$d = (D_{\text{Cu}^+}/D_{\text{Cu}^{2+}})^{2/3} \quad (23)$$

and k is given by

$$k = v^{1/6}/(0.620nFAD_{\text{Cu}^+}^{2/3}\omega^{1/2}N) \quad (24)$$

where ν is the intrinsic viscosity, ω is the rotation rate and N the geometric factor (0.422). The value of K_{eq} can be determined from the slope of a plot of Δi versus $\Delta\omega^{1/2}$. The value of K_{eq} was thus determined to be $4.6 (\pm 0.2) \times 10^{-7}$, which is close to the value of $5.6 (\pm 0.4) \times 10^{-7}$ obtained by Tindell and Bruckenstein. When corrected with activity coefficients from Table I, the final value of K_{eq} was $1.3 (\pm 0.1) \times 10^{-6}$. Correcting the value of Tindell and Bruckenstein for activity coefficients, we obtained a value of $1.2 (\pm 0.1) \times 10^{-6}$.

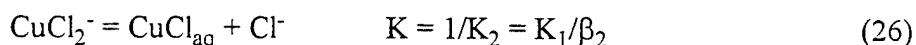
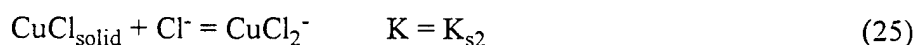
The measurements of Tindell and Bruckenstein were made using a platinum ring electrode, which performs much better in this application than a glassy carbon ring. Thus, with a Pt ring the current can be measured directly rather than employing the differential method employed here. However, the glassy carbon electrode has the advantage of very high overpotential for many organic oxidations and thus displays an acceptable background current in solutions containing significant amounts of organic substances. Thus the method presented here shows general utility for the examination of such systems as mixed solvents and samples of natural waters.

Determination of $E^0(\text{Cu}^+/\text{Cu})$. The values found for E^0_2 and K_{eq} were inserted into eq 19 to yield a value for E^0_1 of $0.273 (\pm 0.006)$ V vs. SCE. This is close to the value of 0.278 V vs. SCE, found in the literature.¹⁰ This is the standard potential which appears in the equations for ψ .

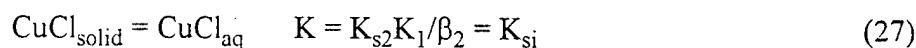
Determination of K_1 and β_2 . The data of Wikiel et al.³ were analyzed as described above. The program converges on optimal values of parameters when reasonable initial estimates are entered. Figure 4 shows a normal pulse voltammogram of a copper microdisk electrode in aqueous 0.05 M chloride solution (0.049 M NaCl + 0.001 M HCl) together with the best-fitting curve. The results of the fit are marginal, judging by the signal-to-noise ratio of 62. However, the values of the stability constants are

unreasonable ($\log K_1 = 3.51$ and $\log \beta_2 = -1.89$). Also, the slope ($-2.081 \mu\text{A}$) is larger than one would expect (e.g., $-0.7 \mu\text{A}$ for $D = 2 \times 10^{-5} \text{ cm}^2/\text{s}$).

Consider the final data point of the voltammogram, taken at $+0.05 \text{ V}$. Using the values of K_1 and β_2 from this fit, the concentrations of species at the electrode surface under these conditions are $[\text{Cu}^+]_s = 170 \mu\text{M}$ (from Nernst equation), $[\text{Cl}^-]_s = 28.3 \text{ mM}$ (from eq 17), $[\text{CuCl}]_s = 15.5 \text{ mM}$ (from the definition of K_1), and $[\text{CuCl}_2^-]_s = 1.8 \text{ nM}$ (from the definition of β_2). Although these values satisfy the equilibrium constants, K_1 and β_2 , they exceed the solubility of the dissolved neutral species CuCl_{aq} . We can calculate the intrinsic solubility of CuCl by combining the equilibrium constants of the following reactions:



Combining these two reactions, we have a reaction for which the equilibrium constant is the intrinsic solubility of CuCl , K_{si} :



Typical values of K_{s2} ,¹⁴ K_1 and β_2 ¹⁵ yield a value of K_{si} of 10^{-4} . This value is consistent with experimental data recorded in chloride concentrations above 1 M .¹⁴⁻¹⁶ However, Ahrland and Rawsthorne¹⁶ found that at lower chloride concentrations, CuCl_{aq} is present in higher concentrations. In treatment of those data, Fritz¹⁴ determined that the concentration of CuCl_{aq} is significantly higher than $100 \mu\text{M}$. We have employed the results of Fritz to calculate an average value of K_{si} for the range of chloride concentrations used in our work (0.05 to 1.0 M) and found that value to be 4×10^{-4} , or $\log K_{\text{si}} = -3.4$. This

means that when the results of our treatment of data predict a value of $[\text{CuCl}]_s$ in excess of 400 μM , solid CuCl should be present, thus rendering this model nugatory.

To avoid this situation, voltammograms like the one shown in Figure 4 were truncated at the point where the intrinsic solubility of CuCl was estimated to be exceeded.

Figure 5 shows a fit of the same voltammogram as in Figure 4, but with the range restricted to the potentials for which CuCl is soluble. The stability constants ($\log K_1 = 2.89$, $\log \beta_2 = 5.44$) lie within the range of values in the literature ($\log K_1$ is between 2.70 and 3.10, $\log \beta_2$ is between 5.19 and 6.06 according to Smith and Martell¹⁵). The signal-to-noise ratio is now 58, which is roughly the same as in Figure 4 despite the fact that the maximal signal is decreased ten-fold. More telling, there is no pattern of residuals in Figure 5, whereas in Figure 4 the deviations are clearly systematic. The slope is close to the predicted value ($-0.5758 \mu\text{A}$). This behavior was observed over the entire range of chloride concentration. Thus the fit can be used to test whether the model applies. In particular, in this case the lack of fit detects formation of solid products not taken into account in the model.

The result of fits to 20 voltammograms is listed in Table II. The average values are $\log K_1 = 2.93 (+0.02, -0.05)$, $\log \beta_2 = 5.54 (+0.12, -0.17)$. These values fall within the range of other literature reports.¹⁵

An activity ratio plot appears in Figure 6, where the activities of the species are divided by the activity of the reference species Cu^+ . The solid lines represent the activity ratios for CuCl for $C = 0.5 \text{ M}$ (d) and 0.05 M (e). Lines b (squares) and c (diamonds) correspond to activity ratios for CuCl_2^- for $C = 0.5 \text{ M}$ and 0.05 M , respectively. Three dashed lines appear as well. The first line (a) corresponds to $\log (K_{\text{sl}}/a_{\text{Cu}^+})$. At the potential where this line intersects the solid lines for CuCl , the voltammograms were truncated. At potentials more negative than the point of intersection, solid CuCl does not exist. As expected, the point of intersection moves to more negative potentials as the

chloride concentration is increased. The intersection occurs at $E = -0.010$ V when $C = 0.05$ M (line g) and $E = -0.065$ V when $C = 0.5$ M (line f).

In addition to the two stability constants, further information is provided by the regression analysis by the COOL algorithm. Recalling eqs 9 and 12, it is apparent that the slope of the regression should equal $-(4nFDrC)f(P)$, and the intercept should be close to zero current. Values of the slope are also presented in Table II. The only unknown in the slope is the product $Df(P)$.

We have calculated D by iteration from the slopes of the regression analyses. Figure 7 shows the calculated diffusion coefficient versus the square root of ionic strength. As specified previously, this diffusion coefficient is an average diffusion coefficient for all three species, Cl^- , CuCl and CuCl_2^- . The dashed line in the figure shows the expected dependence of diffusion coefficient of chloride on the square root of ionic strength for a 1:1 electrolyte based on the equation

$$D = D_0(1 - 0.256I^{1/2}) \quad (28)$$

The reported value of diffusion coefficient for chloride at zero ionic strength¹⁷ is $2.03 \times 10^{-5} \text{ cm}^2/\text{s}$, whereas the value for CuCl_2^- is apparently about one-fourth as large.¹⁸ As we have assumed all diffusion coefficients are equal, this may be responsible for the values of about $0.5 \times 10^{-5} \text{ cm}^2/\text{s}$ we obtain at higher concentrations of chloride. Migration may also influence the apparent value of diffusion coefficient, as discussed below.

Effect of Migration. Three issues need to be addressed concerning the effects of migration. The most obvious, which we will deal with last, is the effect of migration on the amplitude of the response (i.e., the effect on a , eq 18). The second is the effect on the shape of the wave, which will cause systematic deviation from the model for the

anodization reaction. Third is the effect on the position, which will affect only the values of $K_1\theta\gamma$ and $\beta_2\theta\gamma C$.

The dependence of the shape of steady-state voltammetric waves on the concentration of supporting electrolyte has been studied in some depth.¹⁹⁻²¹ We rely upon the treatment of Myland and Oldham,²¹ as it is apparently the most thorough approach to this problem. While these authors specify that their work does not include the case of total absence of supporting electrolyte, all of the relevant equations are applicable when the support ratio (ρ) is chosen to be a sufficiently small number. We have generated theoretical voltammograms according to the procedure of Myland and Oldham and analyzed them with the analysis routine described above. The two reactions $p = 1$ and $p = 2$ are investigated separately.

For $p = 1$, the comparison is straightforward. It is the case of a singly-charged reactant being converted to a neutral product, which in Myland and Oldham's terminology is the case $z = -1$, $n = 1$. A voltammogram was constructed using a value of ρ of 0.0001, and a value of K_1 of 800. The value of K_1 affects only the position of the wave. The voltammogram was normalized by division by the limiting current in the well-supported case. Thus the maximum dimensionless current is 1.98; it is equal to 2 when the support ratio is exactly zero.

To analyze this voltammogram, the value of β_2 was held at 0.01 while the value of K_1 was allowed to vary. The resulting values of K_1 and the slope of the regression depend on where the theoretical voltammogram was truncated. Figure 8 shows the theoretical voltammogram with three representative best-fitting curves. The effect of migration on wave shape is apparent. Numerical results are shown in Table III. When the voltammogram is extended toward the plateau region, the slope of the regression approaches the limit of 1.98. The optimal value of K_1 decreases to values much lower than 800. As the theoretical voltammogram was truncated further and further toward the foot of the wave, the optimal values of K_1 increases to the limit of 800, but the regression

slopes decreases to unity. This shows that migration enhances the current and broadens the wave, but these effects are not significant at the foot of the wave. This finding is consistent with that of Myland and Oldham.²¹ It is therefore safe to say that as long as the wave is truncated to roughly 15% of its maximum height, the influence of migration on both the shape and the amplitude of the $p = 1$ wave can be ignored.

When $p = 2$, the situation is more complicated. To the best of our knowledge, the problem of two singly-charged reactants being converted to a product ion of the same charge has not been solved. However, it is the most important case under our experimental conditions, for which precipitation of CuCl restricts the potential range to values where CuCl_2^- predominates (i.e., the predominant reaction is that with $p = 2$). To approximate this situation, we have likened our case $p = 2$ to Myland and Oldham's case $z = -2$, $n = 1$. The extent to which this case is similar to the $p = 2$ reaction is not clear, but in our estimation it is the most similar case for which a mathematical treatment exists.

A theoretical voltammogram was constructed based on a routine outlined in ref 21. For the purposes of calculating the shape and position of the wave, the following values were chosen: $K_1 = 0$, $\beta_2 = 3 \times 10^5$, $C = 1.0$ M. The voltammogram was normalized by division by the limiting current for $p = 1$, in the presence of a large excess of supporting electrolyte. The ratio of limiting currents without and with excess supporting electrolyte is 1.274.^{20,21} As $p = 2$ (cf. eq 5), the maximum value of the total dimensionless current function is 0.637.

This theoretical voltammogram was truncated at various points and analyzed with the data analysis routine for the anodization reaction. For this analysis, the value of K_1 was held constant at a value close to zero (0.01), and the value of β_2 was allowed to vary. As in the previous example, the results of the regression analysis varied depending on where the voltammogram was truncated. Figure 9 shows a calculated voltammogram together with selected best-fit curves. The results of these analyses are shown in Table IV. The results indicate that as the voltammogram is truncated further and further toward the foot

of the wave, the slope of the regression increases from a value close to the theoretical limit of 1.274 to larger values. At the same time, the optimal values of the formation constant β_2 decrease. The actual values of β_2 cannot be interpreted because of the discrepancy between the two models.

The lack of supporting electrolyte influences the height and the broadening of the wave. These two factors (the limiting ratio and the ohmic polarization) appear explicitly in the procedure of Myland and Oldham. We can therefore quantify these effects. In all cases, the experimental voltammograms were truncated before the value of the ohmic polarization (η_{ohm}) reached 6 mV. Translating this error in potential ($\eta_{\text{ohm}} = E' - E$) into an error in β_2 , we have

$$\beta_2'/\beta_2 = \exp [nf(E' - E)] = \exp [nf(\eta_{\text{ohm}})]$$

$$\leq 1.26$$

(29)

a relationship which arises from the definition of β_2 and the fact that at a given current, the activities of Cl^- and CuCl_2^- are fixed. The factor of 1.26 corresponds to an error of ± 0.10 in the logarithm of β_2 , which is within the standard deviation of our analysis, reported above. Thus we can conclude that for the formation of CuCl_2^- , as was the case with the formation of CuCl , the lack of supporting electrolyte does not seriously distort the voltammetric wave. Of course, the extent to which this situation mimics that of the true $p = 2$ case is unknown. The combined effects of migration and homogeneous reaction have been considered, but the state of development of the treatment of this problem does not permit ready application to the present case.²²

Returning to the discussion of the diffusion coefficient, we cannot determine the extent to which migration is responsible for the values of diffusion coefficient. Figure 7 shows that at higher chloride concentrations, the diffusion coefficients parallel the

theoretical line for Cl^- , although the values are lower. As the chloride concentration decreases, the values for the diffusion coefficient increase sharply. One can see from Figure 6 that the relative amount of CuCl produced at low chloride concentrations is much larger than when the chloride concentration is high. Thus we believe that the higher values of diffusion coefficient at low chloride concentrations are due to the increased significance of CuCl as a product of anodization.

Comparison with Previous Results. We compare the results of this analysis to those of Wikel et al.³ The original analysis did not account for the formation of CuCl in the calculations, nor did it consider the limited solubility of Cu(I) species. The effect of neglecting the formation of CuCl will tend to give values of β_2 which are too high, since all of the observed current is inappropriately considered to contribute to formation of CuCl_2^- . In addition, the value of E°_1 used in that analysis (0.2805 V vs. SCE) was more positive than that determined here. This will result in values of β_2 which are larger than those determined when E°_1 is 0.273 V vs. SCE. On the other hand, neglecting the precipitation of CuCl in the original work led to the inclusion of data points in the analysis which no longer corresponded to the model. The effect of precipitation of CuCl at the electrode surface probably makes the observed current too low, which results in low values of β_2 . From the final result in the original analysis, namely that $\log \beta_2 = 4.9$, it appears that the latter effect was predominant.

An additional virtue of the present method is that it does not rely on fitting a straight line through semilogarithmic plots, which is notoriously subjective. Rather, this data analysis routine makes use of each data point in determining the optimal values of the parameters on which the current function depends.

CONCLUSIONS

The data analysis routine described herein has been used to determine stability constants of CuCl and CuCl_2^- . It can be used in general to determine stability constants for formation of MX and MX_2 from data obtained by anodization of the metal. The approximation is only that the diffusion coefficients of all diffusing species are assumed to be the same. This approximation affords great simplification of the mathematical formulation of the problem. The model treats the entire current range and does not require selection of portions of the data by arbitrary or empirical criteria. In addition to the optimal value of parameters, the analysis yields the signal-to-noise ratio which, together with visual comparison of the data with the best-fitting theory, can be used to assess whether the model accounts for all of the features of the data.

In the present case, ironically, the limited solubility of CuCl made it necessary to truncate the voltammograms well before the theoretical diffusion-limited plateau current was achieved. The experimental system presented here also contained complications due to absence of supporting electrolyte. These complications have been demonstrated to be insignificant in the range of potentials explored. Over the entire range of bulk chloride concentrations used, this routine yielded values of the formation constants which agree well with those found in the literature. Also, in spite of the fact that only a small part of the total voltammetric wave was used, this analysis yielded amplitudes of the total wave which are consistent with theory.

This model is applicable to the anodization of various metals, in the presence of various ligands, where the problem of product solubility may not arise as it did here. Moreover, this routine is not limited to aqueous media, as long as the standard potential of the oxidation of the metal is known. We are presently working on applying a similar treatment for ethylene glycol-water mixtures.⁴ Our aim is to use this technique to analyze the reactions involved in corrosion processes in various complexing media of interest.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research. Portions of the work were carried out at the State University of New York at Buffalo.

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Table I. Calculated Activity Coefficients^{a,b}

[CuSO ₄]/mM	[H ₂ SO ₄]/M	I/mM	$\gamma(\text{Cu}^{2+})$	$\gamma(\text{Cu}^+)$
0.97	0.0463	61.9	0.39	
1.94	0.0453	61.3	0.39	
2.90	0.0444	60.8	0.39	
3.87	0.0434	60.4	0.38	
4.84	0.0425	59.9	0.38	
0.97	0.0165	30.0	0.50	
1.95	0.0124	27.6	0.52	
2.93	0.0103	27.8	0.51	
3.90	0.0082	28.2	0.51	
4.87	0.0062	28.7	0.51	
1.00	0.0089	19.9	0.56	
2.00	0.0069	20.2	0.56	
2.99	0.0049	20.5	0.56	
3.99	0.0020	19.4	0.57	
4.99	0	20.0	0.56	
370	1.4	2180	0.06	0.41

^a From eq 21.^b Calculated for $t = 25\text{ }^{\circ}\text{C}$.

Table II. Equilibrium Constants for Formation of CuCl and CuCl₂⁻.^a

[Cl ⁻] ₀ /M	log K ₁	log β ₂	slope/μA ^b	S/N ^c
0.05	2.89	5.44	-0.576	58
0.05	2.88	5.38	-0.594	59
0.1	2.87	5.48	-0.952	110
0.1	2.89	5.56	-0.967	81
0.2	2.93	5.54	-1.315	104
0.2	2.92	5.49	-1.476	130
0.3	2.94	5.57	-1.369	118
0.4	2.88	5.39	-2.262	109
0.4	2.91	5.55	-1.896	117
0.5	2.91	5.54	-2.574	165
0.5	2.91	5.55	-2.572	173
0.6	2.92	5.55	-2.788	145
0.6	2.92	5.55	-2.591	150
0.7	2.94	5.56	-3.141	163
0.7	2.94	5.59	-3.021	147
0.8	2.90	5.59	-3.354	192
0.8	2.90	5.59	-3.089	150
1.0	3.01	5.81	-2.936	105
1.0	2.98	5.70	-3.226	142
average:	2.93	5.54		
std. dev.:	+ 0.02	+ 0.12		
	- 0.05	- 0.17		

^a The voltammograms were obtained at a 12.5 μm radius copper microdisk electrode in 0.001 M HCl with NaCl added to bring the solution up to the nominal chloride concentration. The solution was thermostated at 25 °C. The pulse time was 50 ms, and the rest pulse was 1 s at a potential at which no current flowed, between -0.4 V and -0.35 V vs. SCE. The voltammograms were analyzed as described in the text.

^b $4nFD[Cl^-]_0\tau f(P)$

^c Span of the current divided by the root-mean-square deviation of the model from the data.

Table III. Results of Analysis of Theoretical Voltammogram ($p = 1$).^a

$E_{\max}/V(\text{SCE})$	K_1	slope/ μA^b	% of maximum height
0.500	203	-1.91	100
0.350	227	-1.85	99.5
0.200	368	-1.60	80.3
0.050	773	-1.03	51.0
-0.100	800	-1.00	15.4

^a The voltammogram was constructed based on the routine published in ref 21, where $\rho = 0$, $z = -1$ and $n = 1$.

^b $4nFD[\text{Cl}^-]_0 \text{rf}(P)$

Table IV. Results of Analysis of Theoretical Voltammogram ($z = -2$).^a

$E_{\max}/V(\text{SCE})$	β_2	slope/ μA^b	% of maximum height
0.200	6.51×10^5	-1.36	100
0.100	5.49×10^5	-1.41	99.8
0.000	3.47×10^5	-1.61	90.6
-0.100	2.16×10^5	-2.09	18.5

^a The voltammogram was constructed based on the routine published in ref 21, where $\rho = 0$, $z = -2$ and $n = 1$. It is intended to approximate the case where two singly-charged reactant ions are converted to yield a single product molecule of the same charge.

^b $4nFD[\text{Cl}^-]_0 \tau(P)$

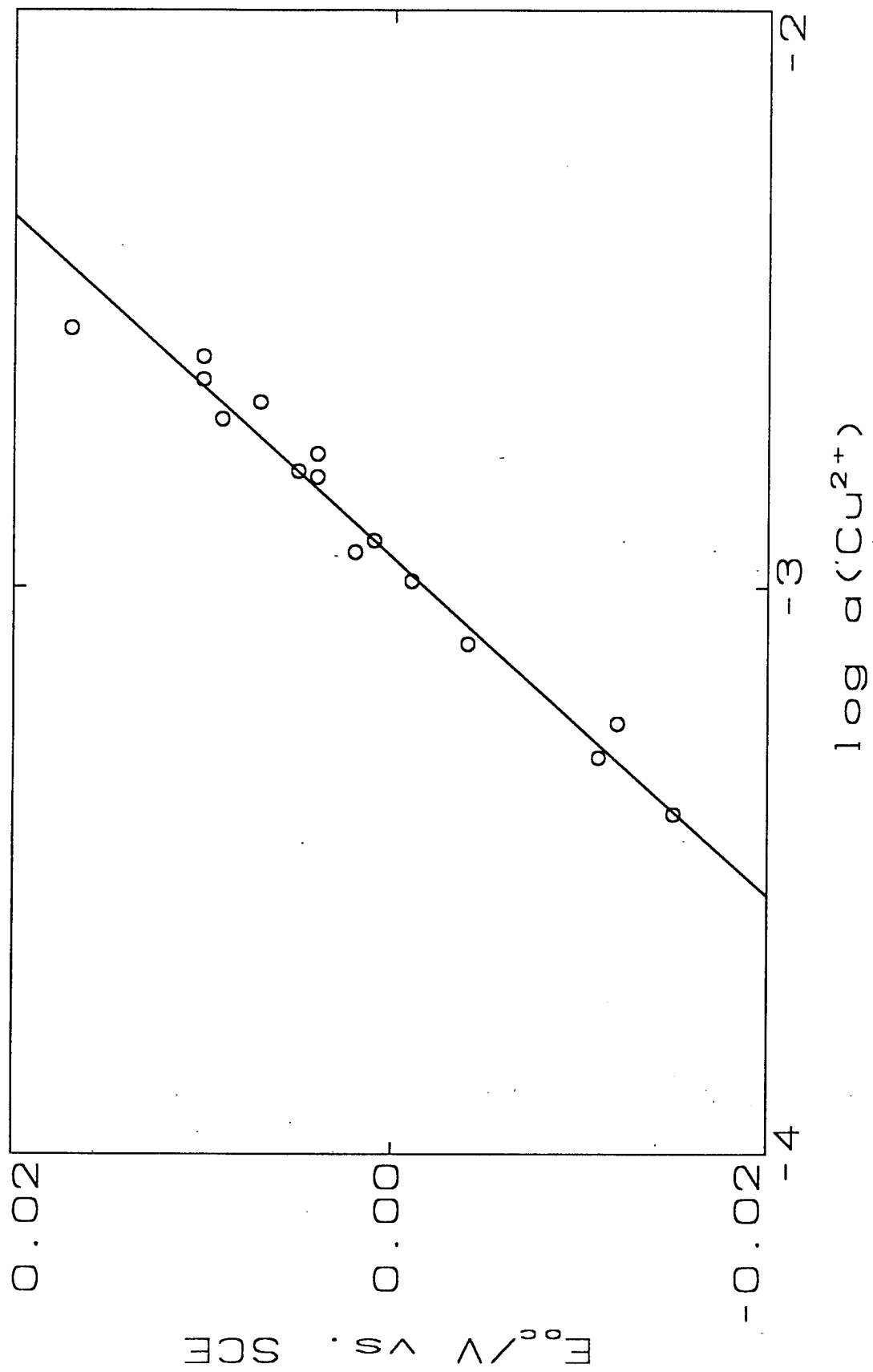
FIGURES

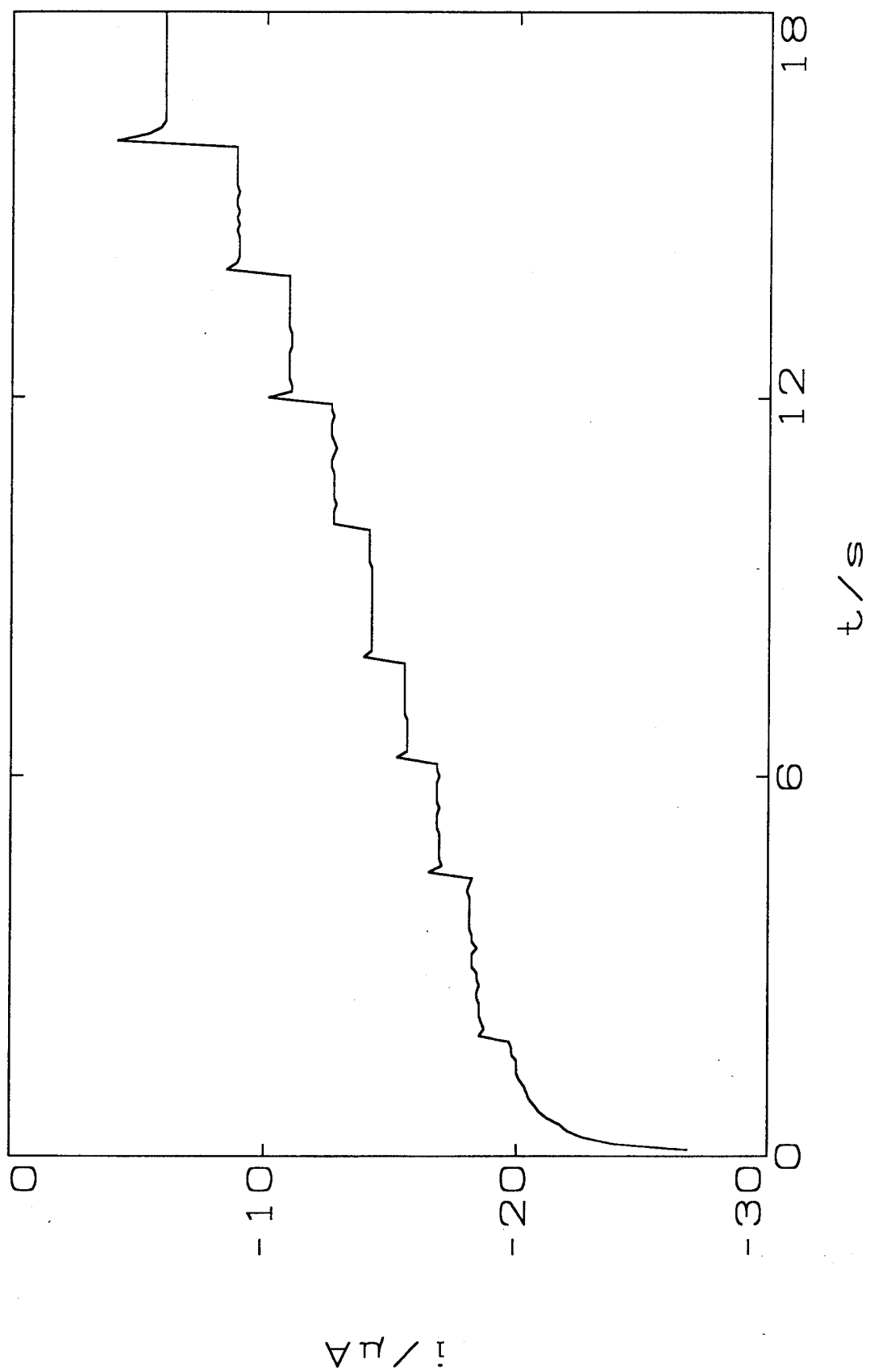
1. Open circuit potentials of a copper wire electrode vs. SCE reference. Activity coefficients were taken from Table I.
2. Current-time trace for a rotation rate-step experiment in which the disk was copper-plated glassy carbon and the ring bare glassy carbon. The solution was the plating solution ($0.37 \text{ M CuSO}_4 + 1.4 \text{ M H}_2\text{SO}_4$). Pt flag counter electrode; $E_r = +0.55 \text{ V vs. SCE}$. Rotation rates from 900 to 100 rpm in 100 rpm steps.
3. Differential current versus differential square root of rotation rate for experiments such as shown in Figure 2.
4. Normal pulse voltammogram (points) with the best-fitting curve. The electrode was a $12.5 \text{ }\mu\text{m}$ -radius copper microdisk, the solution $0.049 \text{ M NaCl} + 0.001 \text{ M HCl}$, the pulse time 50 ms, the rest time 1 s and the rest potential -0.35 V .
5. Same voltammogram as that in Figure 4, but restricted to potential values where CuCl is soluble.
6. Activity ratio diagram plotted as $\log (a_i/a_{\text{Cu}^{2+}})$ versus potential; the species i are (b) CuCl_2^- (for $C = 0.5 \text{ M}$); (c) CuCl (for $C = 0.5 \text{ M}$); (d) CuCl_2^- (for $C = 0.05 \text{ M}$); (e) CuCl (for $C = 0.05 \text{ M}$). Also shown are (a) $\log (K_{\text{si}}/a_{\text{Cu}^{2+}})$, and lines indicating the potential where solid CuCl is present for $C =$ (f) 0.5 M , (g) 0.05 M .

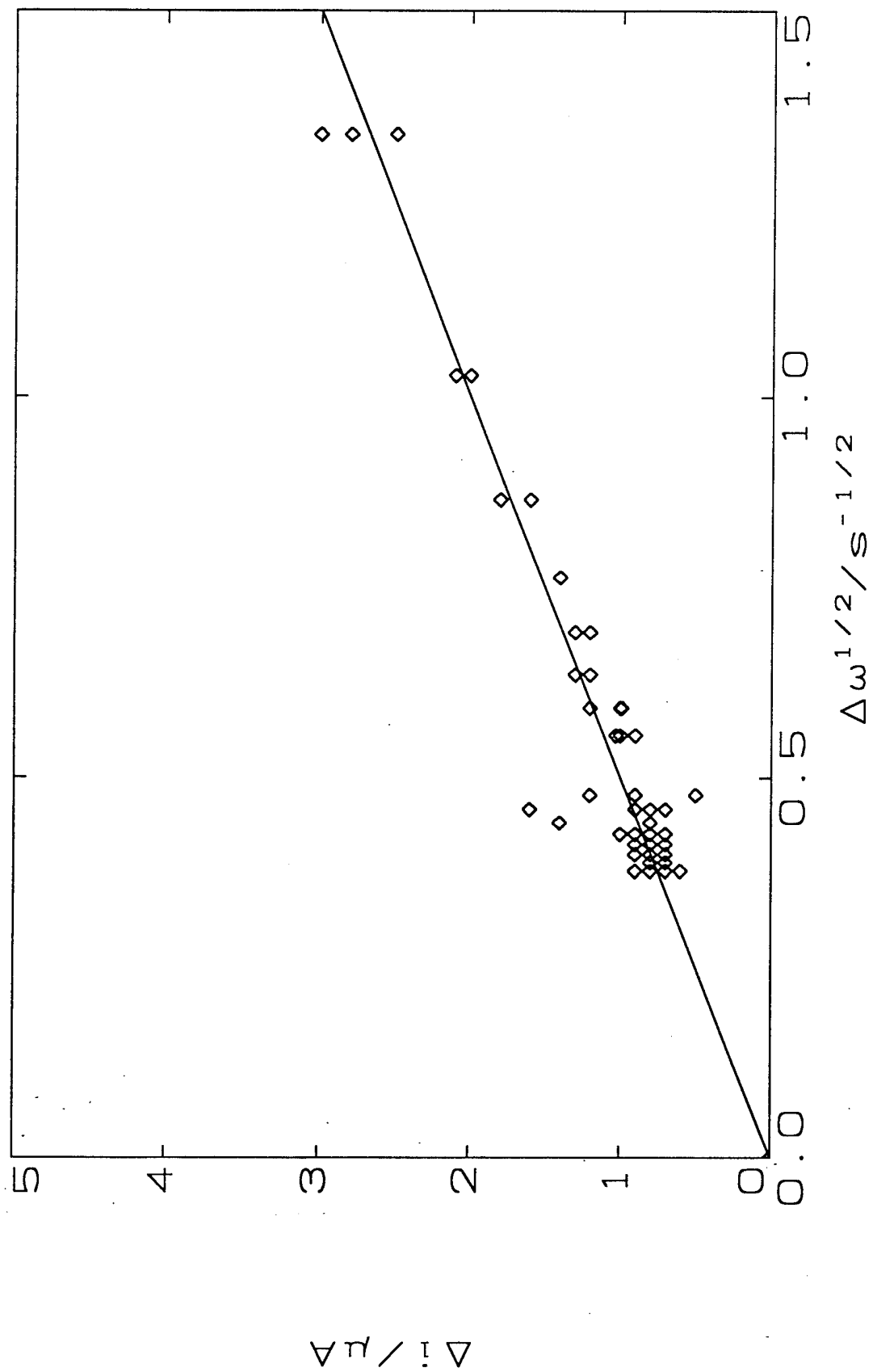
7. Calculated diffusion coefficients (from regression slopes) versus square root ionic strength.

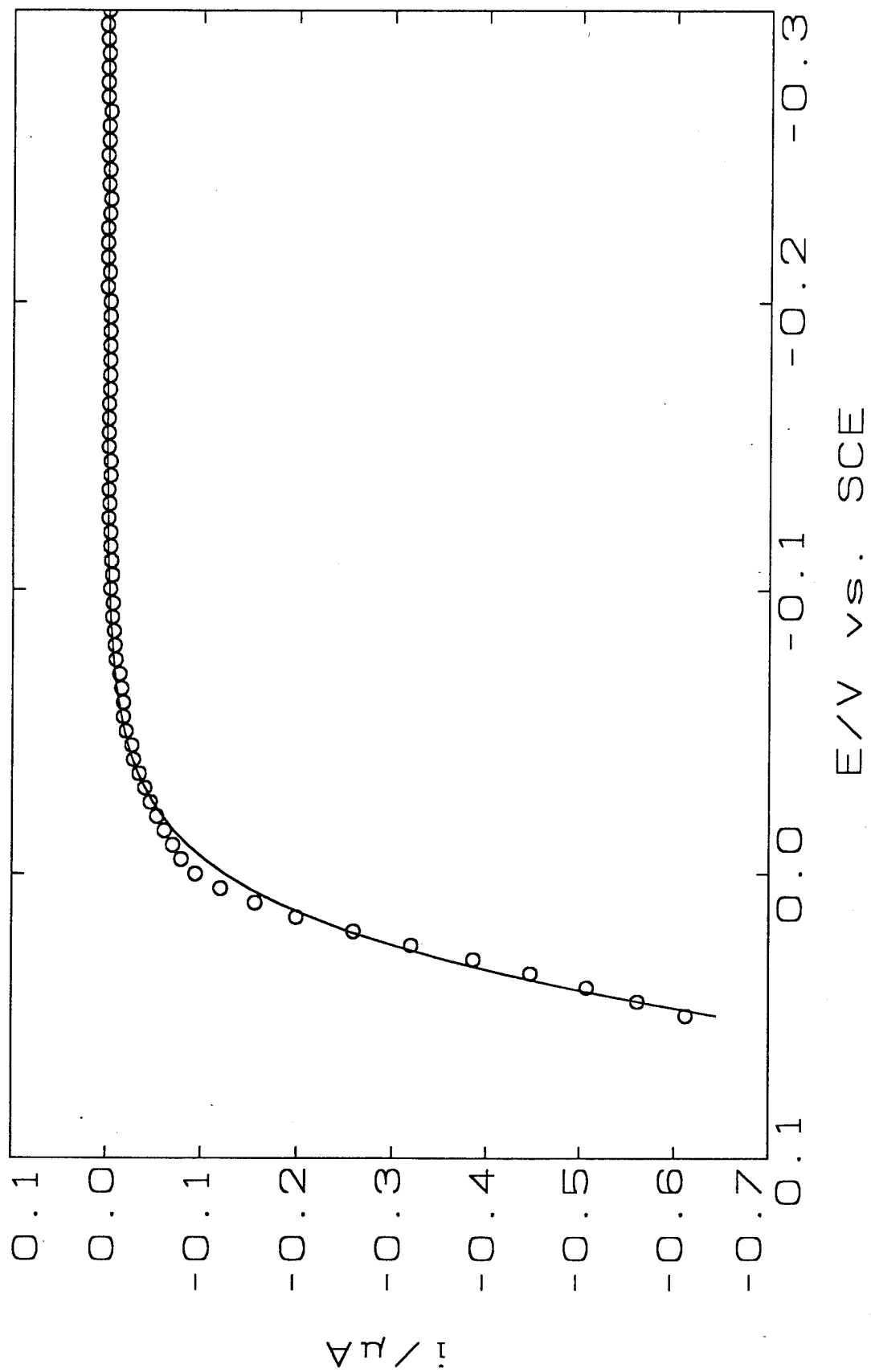
8. Theoretical voltammogram (solid line) based on the treatment described in ref 21, where $\rho = 0$, $z = -1$ and $n = 1$. Also shown are three best-fitting curves, truncated at different potentials, where β_2 has been held constant at a value close to zero; $E_{\max} =$ (a) 0.500, (b) = 0.200, (c) = 0.050 V vs. SCE.

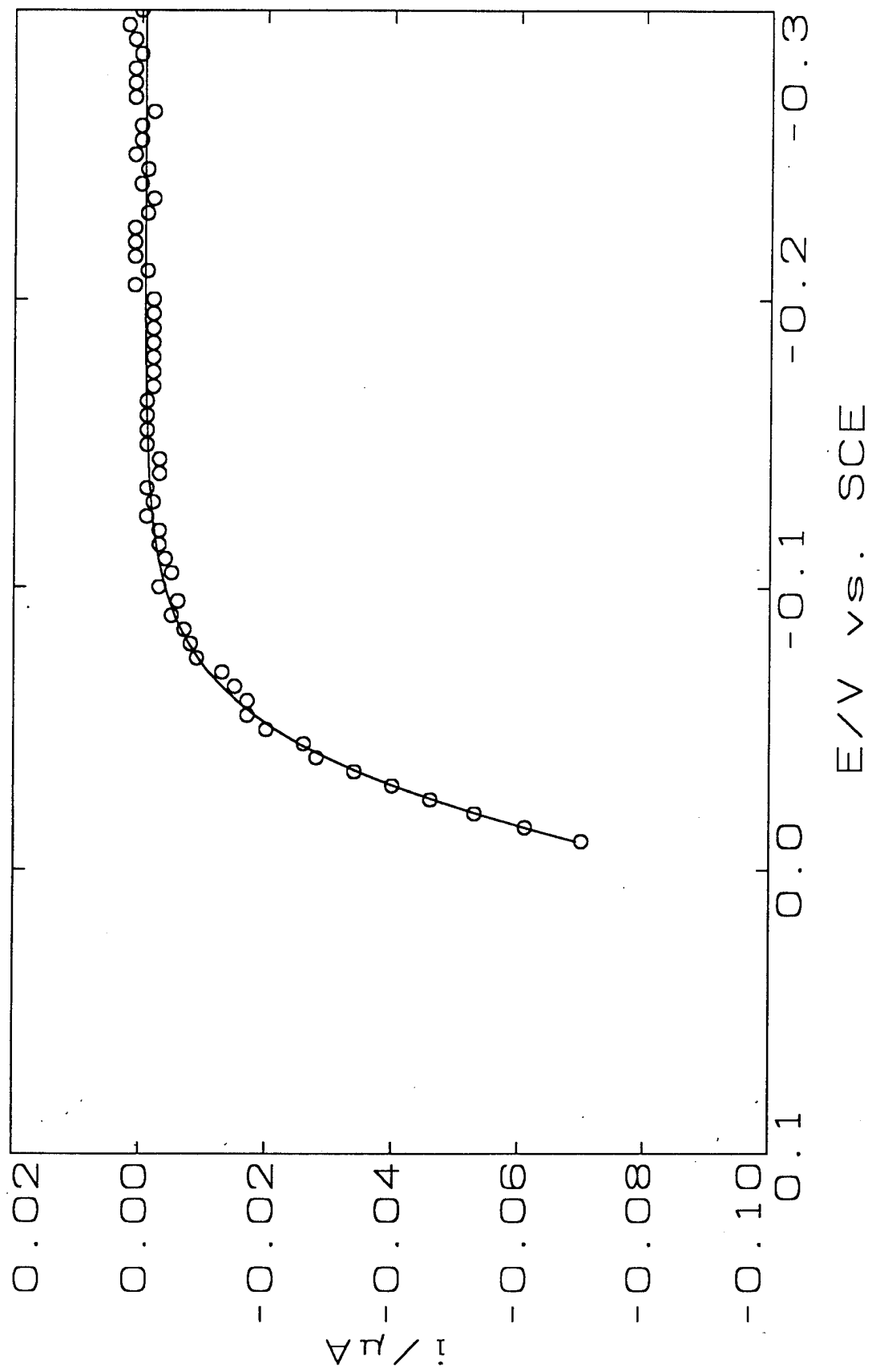
9. Theoretical voltammogram (solid line) based on the treatment described in ref 21, where $\rho = 0$, $z = -2$ and $n = 1$. Also shown are three best-fitting curves, truncated at different potentials, where K_1 has been held constant at a value close to zero; $E_{\max} =$ (a) 0.200, (b) = 0.100, (c) = 0.000 V vs. SCE.

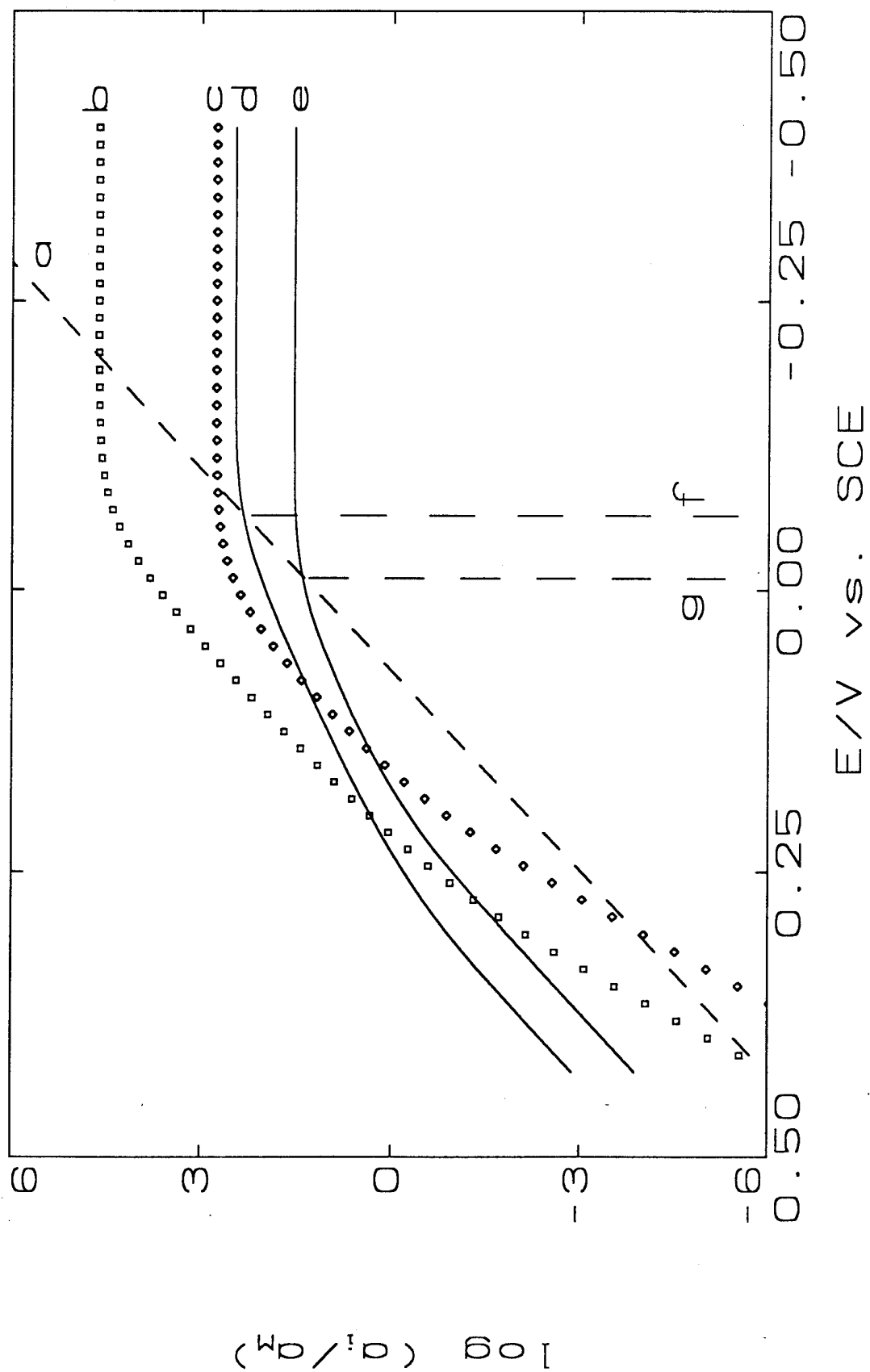


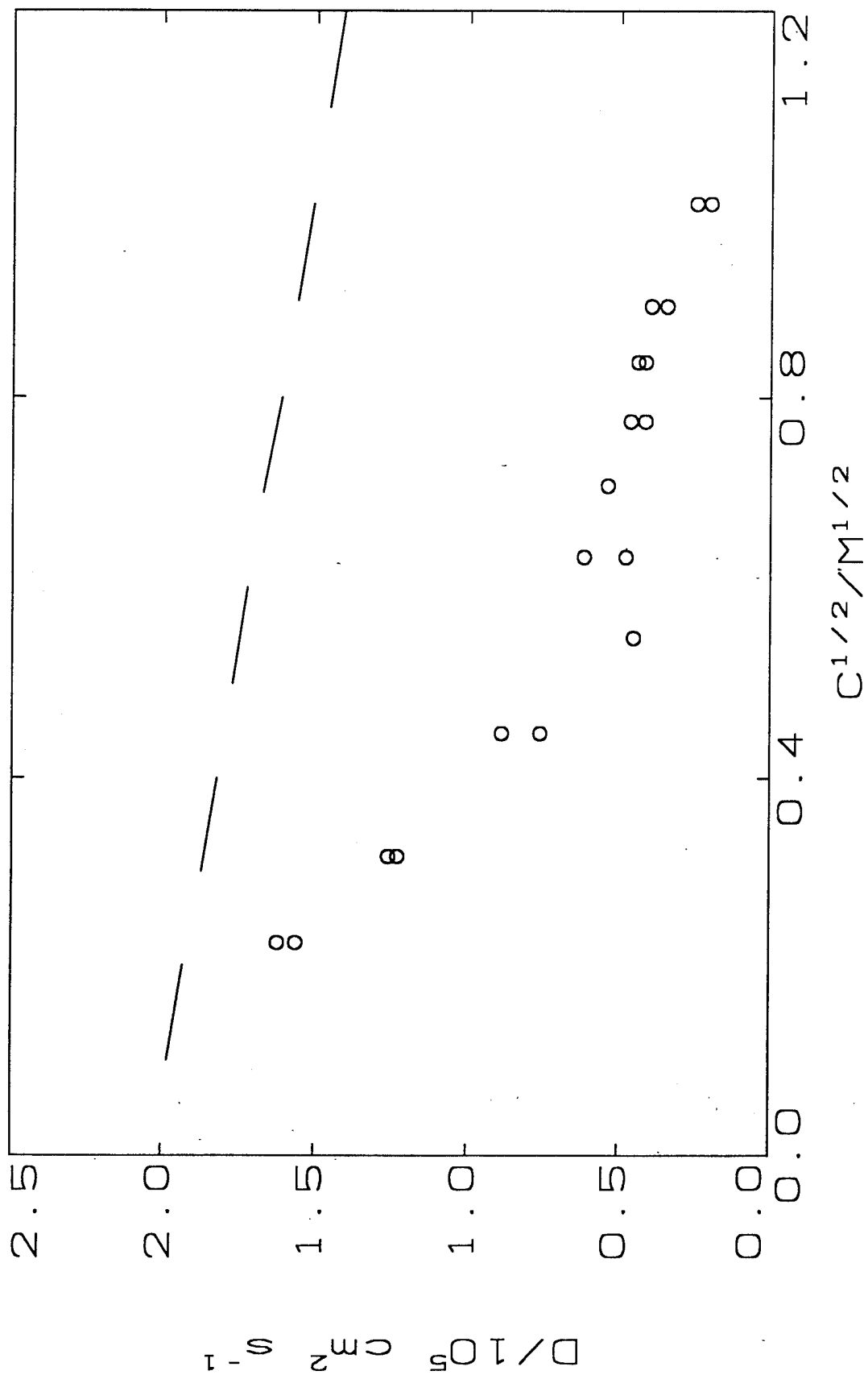


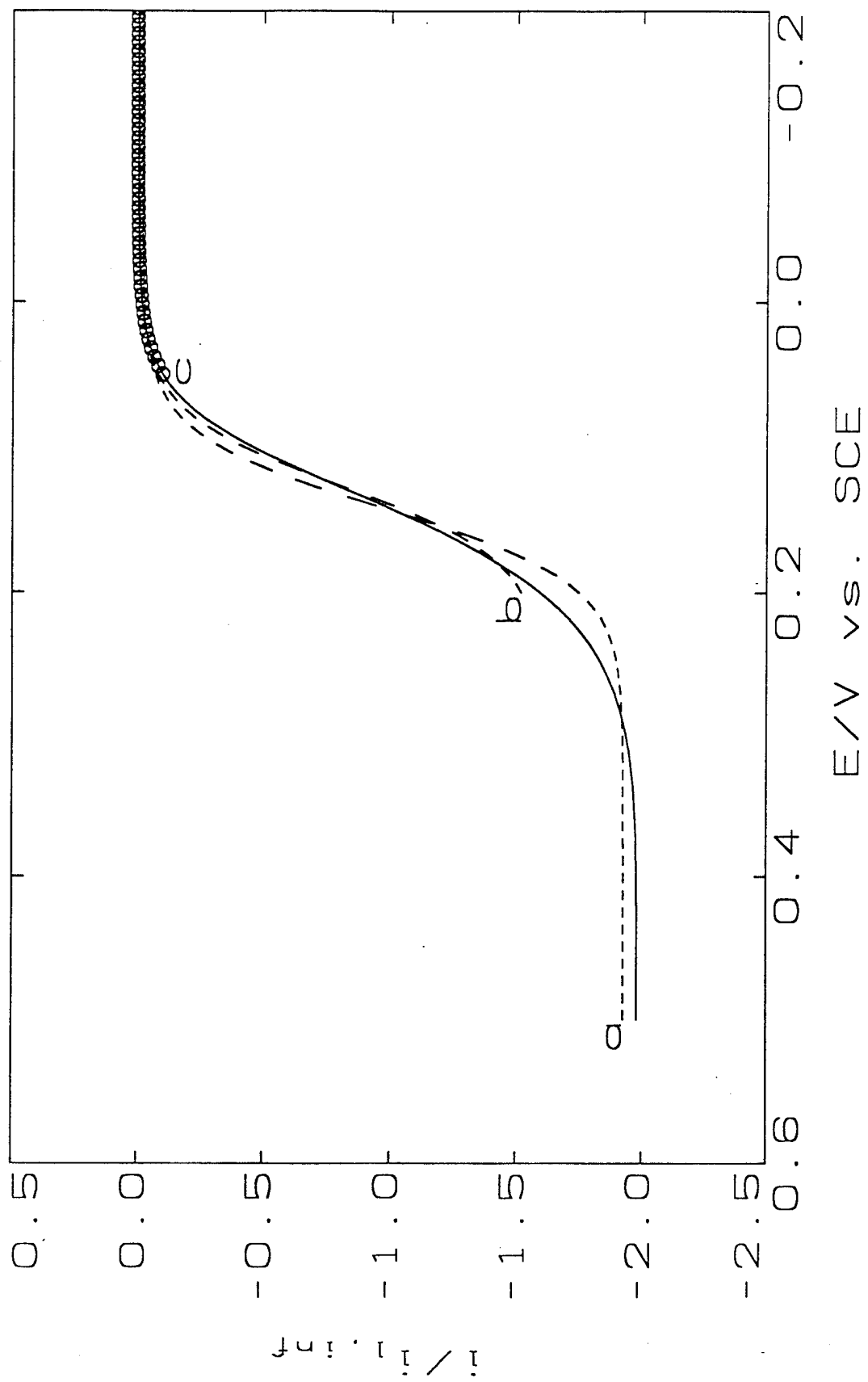


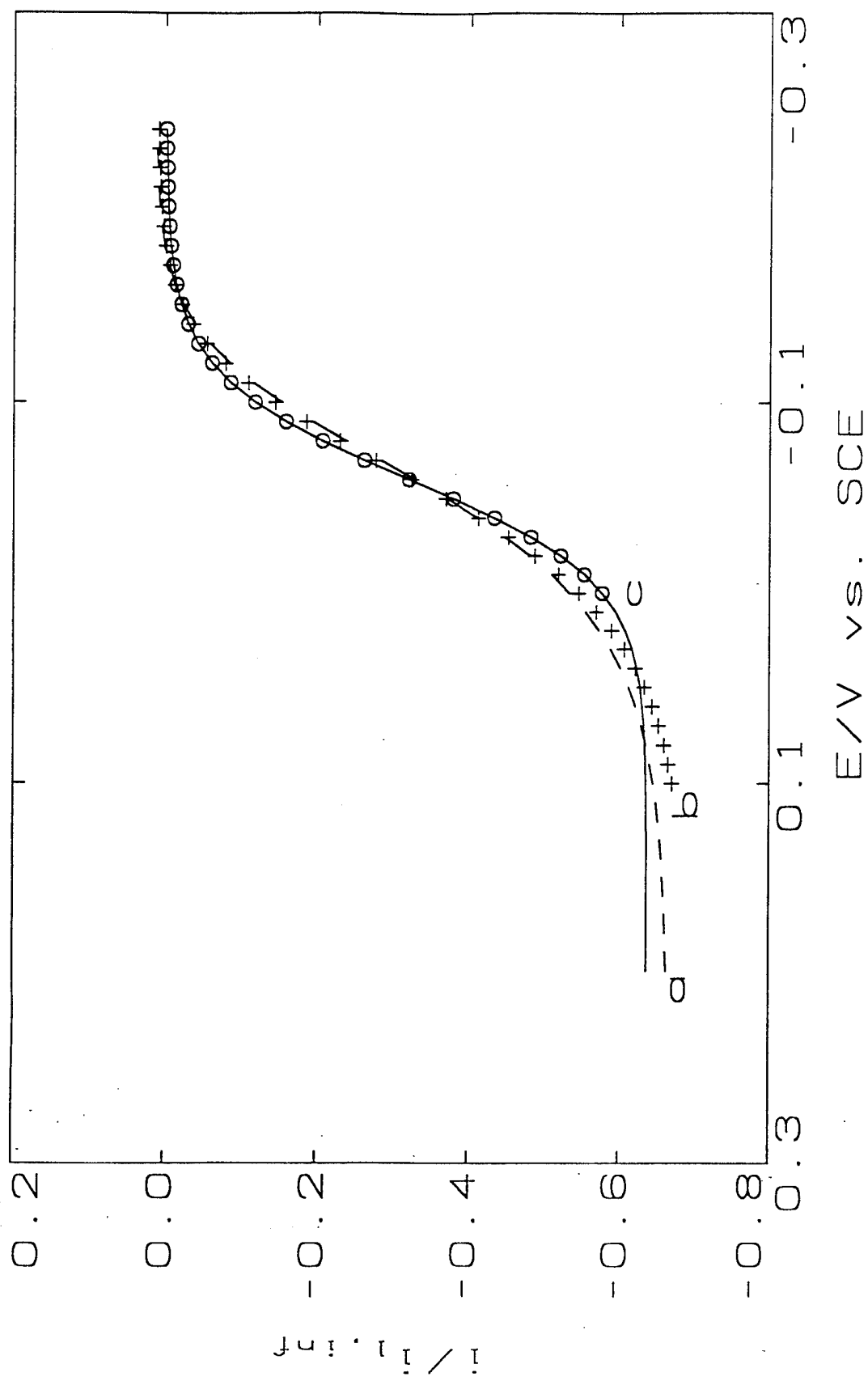












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